



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>D01D 1/06, D01F 1/02, 1/04</b> <b>D01F 6/60</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/07120</b> <b>(43) International Publication Date:</b> 30 April 1992 (30.04.92)
<b>(21) International Application Number:</b> PCT/US91/07239 <b>(22) International Filing Date:</b> 10 October 1991 (10.10.91) <b>(30) Priority data:</b> 597,403                      15 October 1990 (15.10.90)      US <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). <b>(72) Inventors:</b> FALLAHA, Fahed, Habib ; 42 Cloverhill Avenue, Drumahoe, Londonderry BT47 3SH (US). LEE, Kiu-Seung ; 4120 October Road, Richmond, VA 23234 (US). <b>(74) Agents:</b> SULLIVAN, Daniel, W. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> METHOD OF MIXING ADDITIVE SOLUTIONS INTO PARA-ARAMID DOPE STREAMS  <b>(57) Abstract</b>  A method of continuously mixing a low viscosity, additive solution stream with a relatively high viscosity, liquid crystalline, para-aramid, spinning dope stream is disclosed. The method comprises introducing the low viscosity stream into the center of the high viscosity stream, and mixing the streams in a static mixer unit.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU <sup>+</sup>	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE*	Germany	MC	Monaco	US	United States of America
DK	Denmark				

<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

TITLE  
METHOD OF MIXING ADDITIVE SOLUTIONS INTO  
PARA-ARAMID DOPE STREAMS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to continuously mixing a low viscosity, additive solution stream with a relatively high viscosity, liquid crystalline, fiber-spinning dope. More particularly, this invention concerns continuously mixing a low viscosity, additive solution stream into a relatively high viscosity, liquid crystalline, para-aramid, spinning dope stream in order to produce a modified spinning dope. The modified spinning dope can be used to spin a high strength, high modulus, para-aramid fiber which is uniformly modified with additives such as colorants, ultraviolet (UV) light screeners, antioxidants, plasticizers, flame retardants, and other property enhancing materials.

Description of the Prior Art

As disclosed in Blades, United States Patent, 3,869,429, methods for preparing high strength, high modulus, aramid fibers are known. However, it is extremely difficult to prepare high strength, high modulus, para-aramid fibers having uniformly distributed additives.

Moulds et al., British Patent, 1,438,067 discloses wet spinning poly(p-phenylene terephthalamide) fibers into a coagulating bath to form water-swollen fibers and then treating the fibers with an aqueous impregnant solution. The reference discloses using impregnants selected from the group consisting of antioxidants, ultraviolet (UV) light screeners, dyes, flame retardants, and antistats.

Milford, Jr., United States Patent, 3,888,821 discloses wet spinning poly(p-phenylene terephthalamide) fibers and then treating the wet, never dried fibers with

an aqueous mixture of ultraviolet (UV) light screener.

Lazarus et al., United States Patent, 4,070,342 discloses a method of injecting a dispersion of a polymer additive in liquid polyisobutene into a transfer line carrying a polyethylene terephthalate polymer melt. The dispersion and polymer melt are then mixed in a stationary mixer immediately before the polymer passes to a spinning block.

Gray, United States Patent, 4,068,830 discloses a method of injecting a low viscosity liquid, water, near the center of a flow pipe into a flowing stream of high viscosity liquid, corn syrup, and then passing said liquids through perforated plates before mixing them in a static mixer.

Copending, coassigned United States Patent Application Serial No. 07/226,645, filed August 1, 1988 to Lee, discloses colored high strength, high modulus, para-aramid fibers and a process for preparing such fibers comprising the steps of: (1) agitating a mixture of an organic pigment, sulfuric acid, and para-aramid polymer, (2) heating the mixture, (3) extruding the solution through a spinneret, (4) passing the extrudate into an aqueous coagulation bath, and (5) washing the newly formed filaments with water and/or alkali.

However, the foregoing references do not disclose injecting a low viscosity, additive solution stream into a relatively high viscosity, liquid crystalline, fiber-spinning dope stream. There are significant differences between such anisotropic spinning dopes and isotropic spinning solutions or melts. For example, because of the anisotropic spinning dope's highly crystalline nature, additives cannot easily penetrate; thus, a method for uniformly mixing the additives with such a dope is needed.

#### SUMMARY OF THE INVENTION

The present invention provides a method of

continuously mixing a low viscosity, additive solution stream with a relatively high viscosity, liquid crystalline, fiber-spinning dope.

An additive solution stream having a viscosity in the range of 5 to 100 centipoise at 50°C, preferably an organic pigment solution stream, and a liquid crystalline, para-aramid, spinning dope stream having a viscosity in the range of 500 to 5000 poise at 80°C are prepared. Preferably, the para-aramid spinning dope stream is poly(p-phenylene terephthalamide). The additive solution stream is then introduced continuously into the center of the para-aramid spinning dope stream. The streams are then uniformly mixed in a static mixer unit having at least one stationary mixing element and a length to diameter ratio of 5. Preferably, the static mixer unit has 2 to 4 stationary mixing elements and a length to diameter ratio in the range of 10 to 20. The volumetric flow ratio of additive solution stream to para-aramid dope stream is in the range of 0.001 to 0.4, and the viscosity ratio of the spinning dope stream to the additive solution stream is in the range of 500 to 100,000.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to continuously mixing a low viscosity, additive solution with a relatively high viscosity, liquid crystalline, para-aramid spinning dope. The spinning dope can be used to spin a high strength, high modulus, para-aramid fiber which is highly modified with additives.

An additive solution is first prepared by techniques known in the art. These additive solutions may include, for example, organic pigments, ultraviolet (UV) light screeners, antioxidants, plasticizers, flame retardants, and other property enhancing materials with minimal transition time. Preferably, the additive solution is an organic pigment solution, and the pigment is at least one selected from the group consisting of (1) monoazo and

diazo pigments, (2) anthanthrone pigments, (3) idanthrone pigments, (4) pyranthrone pigments, (5) vilanthrone pigments, (6) flavanthrone pigments, (7) quinacridone pigments, (8) dioxazine pigments, (9) indigoid and thioindigoid pigments, and (10) isoindolinone pigments.

The preferred monoazo pigment is Colour Index Pigment Red 3. The preferred diazo pigment is Colour Index Pigment Red 242. The preferred anthanthrone pigment is Colour Index Pigment Red 168. The preferred idanthrone pigment is Colour Index Pigment Blue 60. The preferred pyranthrone pigment is Colour Index Pigment Orange 40. The preferred vilanthrone pigment is Colour Index Pigment Blue 65. The preferred flavanthrone pigment is Colour Index Pigment Yellow 24. The preferred quinacridone pigment is Colour Index Pigment Red 122. The preferred dioxazine pigment is Colour Index Pigment Violet 23. The preferred indigoid and thioindigoid pigments are Colour Index Pigment Red 88 and Colour Index Pigment Red 86, respectively. The preferred isoindolinone pigment is Colour Index Pigment Yellow 173.

The foregoing organic pigments are those named in the Colour Index published by the Society of Dyers and Colourists.

The purely organic pigments which are suitable for use in the present invention are soluble in sulfuric acid having a concentration of at least 98%, but are insoluble in water or organic solvents and do not degrade appreciably in 98% sulfuric acid at 95°C when held at that temperature for three hours. Indications of pigment degradation include change of color in the final fiber, bleeding of the pigment into the coagulation bath, and precipitation of the pigment from the spinning dope. Different pigments can be used to generate different colored solutions and the amount of pigment used will depend upon the type of pigment and the amount of tint desired. However, generally, the amount of pigment level should be in the range of 0.01 to 6.0

percent based on total weight of the fiber. All additive solutions should have a viscosity in the range of about 5 to 100 centipoise at 50°C.

The para-oriented aromatic polyamides, (para-aramids), which are useful in the present invention are those described in United States Patent, 3,869,429 in which rigid radicals are linked into polymer chains by amide groups. The chain-extending bonds of the rigid radicals are either coaxial or parallel and oppositely directed. The rigid radicals may be single-ring radicals, multi-ring radicals in which the chain-extending bonds are para-oriented, fused ring radicals, or heterocyclic radicals. Preferred rigid radicals are 1,4-phenylene, 2,6-naphthalene, 1,5-naphthalene, 4,4'-biphenylene, trans-1,4-cyclohexylene, trans-trans-4,4'-bicyclohexylene, and 1,4-pyridylene linked together by trans-vinylene, ethynylene, azo, or azoxy groups. The polyamides may be substituted with simple groups such as chloro- and methyl groups. Both homopolymers and copolymers are suitable as long as the rigid radicals are as defined above. Up to 5 mole percent of non-conforming radicals may be included. The polyamides may be prepared by reaction of a suitable aromatic acid halide with a suitable aromatic diamine in a non-reactive amide solvent which may contain solubilizing salts such as LiCl or CaCl<sub>2</sub>. The polyamide should have an inherent viscosity of at least 4.

The para-aramid polymer is then mixed with cold sulfuric acid having a concentration of at least 98% to provide when heated a dope having a para-aramid concentration of at least 18%. The dope is heated to 80-105°C with stirring and then degassed. The hold-up time of the dope may be 1 to 3 hours in a commercial spinning process. The liquid crystalline spinning dope stream should have a viscosity in the range of 500 to 5000 poise at 80°C. Preferably, the liquid crystalline spinning dope stream is poly(p-phenylene terephthalamide).

The additive solution stream is then introduced continuously into the center of the liquid crystalline, para-aramid spinning dope on line in a standard commercial spinning process. The additive solution stream may be conveniently introduced into the spinning dope by a positive displacement pump at an injection pressure in the range of 200 to 1500 psig, but it is important that the additive solution is introduced into the center of the spinning dope. The volumetric flow ratio of additive solution stream to para-aramid, spinning dope stream should be in the range of 0.001 to 0.4. The viscosity ratio of para-aramid spinning dope stream to additive solution stream should be in the range of 500 to 100,000. The streams are then mixed together in a static mixer unit. A suitable static mixer unit for the present invention has at least one stationary mixing element placed lengthwise in a pipe. These mixing element or elements form intersecting channels that split, rearrange, and recombine the component streams into smaller layers until one homogeneous stream is obtained.

The static mixer unit must be able to sufficiently mix high viscosity streams with low viscosity streams. A static mixer unit having at least one stationary mixing element and a length to diameter (L/D) ratio of five (5) is required, where L is the length of the mixer unit from entrance to exit and D is its diameter. A static mixer unit having 2 to 4 stationary mixing elements with a L/D ratio in the range of 10 to 20 is preferred. As the streams pass through the static mixer unit, there should be a decrease in pressure of at least 50 psig with a decrease lower than 500 psig being more desirable. A "SMX" Static Mixer Unit having at least one stationary "SMX" mixing element with a L/D ratio of 5 is a suitable unit and is available from Koch Engineering Company, Inc. Each "SMX" mixing element is designed primarily for laminar flow of the streams and has open intersecting channels at 45°

relative to the pipe's axis. The mixing elements may be constructed of materials such as carbon steel, stainless steel, "Monel", "Alloy" 20, titanium, "Hastelloy", polyethylene, polypropylene, "Teflon", or "Kynar".

The spinning dope stream is then extruded through a spinneret, collected, washed, and dried by techniques known in the art to yield high strength, high modulus, para-aramid fiber which is uniformly modified with additives. By the term, high strength, it is meant a yarn or filament having a tenacity of at least 18 gpd (15.9 dN/tex). By the term, high modulus, it is meant a yarn or filament having a modulus of at least 400 gpd (354 dN/tex). In the following examples, parts, ratios, and percentages are by weight, unless otherwise indicated

#### EXAMPLE ONE

A pigment solution was prepared as follows:

5 parts of an organic pigment powder mixture, Sandorin Yellow VRL, available from Sandoz Chemical Co., having the pigments, Sandorin Blue RL (Pigment Blue 60)/ Sandorin Scarlet 4RF (Pigment Red 242)/ Sandorin Yellow (Pigment Yellow 24) in a ratio of 15/3/0.5, respectively, was added to 95 parts of 100% concentrated sulfuric acid in a mixing vessel at room temperature. The mixture was stirred until the pigment powder mixture was completely dissolved in the sulfuric acid. The pigment solution was then circulated as a stream, on line, through a filter and pressure control valve and injected at a pressure of 800 psig through a positive displacement pump into the center of a para-aramid spinning dope stream.

The spinning dope stream was a solution of 19.5% poly(p-phenylene terephthalamide) in sulfuric acid. The dope was prepared by completely dissolving 19.5 parts of poly(p-phenylene terephthalamide) polymer having an inherent viscosity of 6 in 80.5 parts of 100% concentrated sulfuric acid at a temperature of 85°C and then degassing

the dope. At this temperature, the spinning dope stream had a liquid crystalline structure.

The streams then entered a "SMX" Static Mixer unit having 4 individual "SMX" mixing elements, each having a length to diameter (L/D) ratio of 5. The static mixer unit was 20 inches in length and had an inside diameter of 0.62 inches, an outside diameter of 0.84 inches, and a total L/D ratio of 20. Such a unit is available from Koch Engineering Company, Inc. The volumetric flow ratio of pigment solution stream to spinning dope stream was 1:25, or 0.04. The viscosity ratio of spinning dope stream to pigment solution stream at 85°C was 1000 poise to 5 centipoise, or 20,000. As the streams passed through the static mixer unit, there was a decrease in pressure of 120 psig.

The mixed stream was then supplied to a metering pump and extruded through a 1000 hole spinneret having capillaries of 0.063 mm in diameter and finally through an air gap of 0.7 cm length into an aqueous coagulation bath at 5°C. The extruded dope was stretched to 6.3 X its original length in the air gap. The resulting fiber was further washed with dilute aqueous alkali and water, dried on a roll at 180°C, and wound up at 713 m/min. The amount of pigment was 1% based on the total weight of the fiber.

The fiber obtained in this example showed a completely uniform distribution of colorants throughout its cross section.

#### COMPARATIVE EXAMPLE ONE

The same procedures as described in EXAMPLE 1 were performed, except that the pigment solution stream was injected into the spinning dope stream through the side of the static mixer unit rather than into the center of the stream. The fiber could not be spun due to continuous drips from the spinneret. These drips were believed to be the result of complete separation of the pigment solution stream from the para-aramid dope.

EXAMPLE TWO

The same procedures as described in EXAMPLE 1 were performed, except that the L/D ratio of the static mixer unit was reduced from 20 to 10 by removing two "SMX" mixing elements. The fiber showed the same uniform colorant distribution as the fiber in EXAMPLE 1.

COMPARATIVE EXAMPLE TWO

Colored fiber was produced by the same process as described in EXAMPLE 2, except that all of the mixing elements in the static mixer unit were removed. The spun fiber showed streaks along its axis indicating very nonuniform mixing of the pigment solution and para-aramid dope.

CLAIMS:

1. A method of mixing a low viscosity, additive solution stream into a high viscosity, liquid crystalline, fiber-spinning dope stream comprising the steps of:
  - (a) preparing an additive solution stream having a viscosity in the range of 5 to 100 centipoise at 50°C;
  - (b) preparing a liquid crystalline, para-aramid, spinning dope stream having a viscosity in the range of 500 to 5000 poise at 80°C;
  - (c) introducing the additive solution stream continuously into the center of the liquid crystalline, para-aramid, spinning dope stream where the volumetric flow ratio of the additive solution stream to the dope stream is in the range of 0.001 to 0.4, and the viscosity ratio of said dope stream to said additive solution stream is in the range of 500 to 100,000; and
  - (d) mixing the additive solution stream and liquid crystalline, para-aramid, spinning dope stream in a static mixer unit having at least one stationary mixing element and a length to diameter ratio of 5.
2. A method in accordance with claim 1 wherein the additive solution stream is pigment solution.
3. A method in accordance with claim 1 wherein the para-aramid spinning dope is poly(p-phenylene terephthalamide).
4. A method in accordance with claim 1 wherein the additive solution is pigment solution, and the para-aramid spinning dope is poly(p-phenylene terephthalamide).
5. A method in accordance with claim 1 wherein the static mixer unit has 2 to 4 stationary mixing elements and a length to diameter ratio in the range of 10 to 20.
6. A method in accordance with claim 4 wherein the static mixer unit has 2 to 4 stationary mixing elements and a length to diameter ratio in the range of 10 to 20.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/07239

**I. CLASSIFICATION OF SUBJECT MATTER** (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D01D1/06; D01F1/02; D01F1/04; D01F6/60

**II. FIELDS SEARCHED**Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int.Cl. 5

D01D ; D01F

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>**III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>**

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US,A,2 934 448 (THEODORE E. PATTON) 26 April 1960 see column 1, line 46 - line 56 see column 2, line 2 - line 4; claims ---	1-6
Y	EP,A,0 295 672 (E.I. DU PONT DE NEMOURS AND CO.) 21 December 1988 see claims ---	1-6
Y	PATENT ABSTRACTS OF JAPAN vol. 7, no. 100 (C-164)28 April 1983 & JP,A,58 025 376 ( NIHON KOUATSU DENKI KK ) 15 February 1983 see abstract ---	1-6
Y	EP,A,0 356 579 (E.I. DU PONT DE NEMOURS AND CO.) 7 March 1990 see claims ---	1-6
	--- -/-	

<sup>10</sup> Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

<sup>11</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>12</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>13</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>14</sup> document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

14 FEBRUARY 1992

Date of Mailing of this International Search Report

25.02.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

TARRIDA TORRELL J.B.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	EP,A,0 074 414 (KANEKAFUCHI KAGAKU KOHIO KK) 23 March 1983 see claim 1 ---	1-6
Y	US,A,4 068 830 (JOSEPH B. GRAY) 17 January 1978 see column 2, line 4 - line 8; claims; figure 1 cited in the application ---	1-6